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Error Analysis in Fe-Rich Geological Samples by X-Ray Fluorescence Spectrometric Analysis: Fundamental Parameter Method

Master's Thesis

(30ECTS)

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List of abbreviations

XRF	X-Ray Fluorescence Spectrometry
WDXRF	Wavelength Dispersive X-Ray Fluorescence Spectrometry
EDXRF	Energy Dispersive X-Ray Fluorescence Spectrometry
XRD	X-Ray Diffraction
ICDD	International Centre for Diffraction Data
FP	Fundamental Parameter Method
SQX	Standardless Analysis Program
PHA	Pulse Height Analyzer
CRM	Certified Reference Materials
RMS	Root Mean Square
σ-est	Standard Error Estimate
LOI	Loss on Ignition

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INTRODUCTION

X-ray Fluorescence spectrometry (XRF) is an analytical technique for the analysing chemical composition of varying types of material-matrices. XRF can also determine thickness and composition of coatings. It's a fast, non-destructive, accurate and precise method with minimal sample preparation. In addition, it does not extensive training or experience on the part of the analyst. XRF is a proven analytical tool in cement, polymer, mining, semi-conductor, wastewater, and pharmaceutical industries. XRF is also widely used in geology and mining. The chemical composition of rocks are used to solve numerous geological problems, including crystallization history of igneous bodies such as granite or basalt, processes of formation of the sea floor, nature of chemical weathering in various climate, stratigraphic correlation of sedimentary and volcanic rocks, processes of ore generation and many others (La Tour,1989) besides of major elements minor and trace elements can be analysed by XRF method. XRF spectrometry is principally divided into Energy Dispersive X-Ray Fluorescence spectrometry (EDXRF)which can typically measure elements from Na to U and Wavelength Dispersive X-Ray Fluorescence spectrometry (WDXRF)which can measure from Be to U with concentration range from sub part per million to 100%. whereas elements with high atomic number have better limit of detection with XRF than light elements. While being a technique of choice of most petrologist and geochemist to obtain rock analyses, it has several limitations, especially when no or minimum sample preparation is done. Principally, XRF measurements can be done without any preparation from the surface of natural rock or sediments e.g. using handheld EDXRF spectrometer. Its is also that XRF analyses were obtained on a finely ground rock powder pressed into coherent pellets. Its is a simple and cost-effective preparation method. However, samples prepared this way suffers from surface roughness, grain size and mineralogical effect. Mineralogical effect is especially significant when dealing with geological samples with difficult matrices like Fe, Al or P ricks rocks and sediments. Alternatively, sample preparation can be done by solution of rock in borate glass. The borate fusion method produces homogenous sample that are easy to handle, can be analysed many times without deterioration, eliminate grain size, mineralogical effect and reduce differences in ass absorption from sample to sample. However, the borate fusion method is not suitable for certain rock types, e.g. sulphidic ores and can be complicated in high Fe and high Al sediments.

Laterite is a residual sediment typically rich in Fe and Al. It is formed under tropical weathering conditions-high temperature and rainfall. Principally it is composed of goethite, hematite, kaolin,

Al-oxyhydroxides, quartz plus other clay materials. In a broader sense, Charman,1998 classified laterite as highly weathered natural material with high concentration of hydrated oxides of Fe and Al due to residual accumulation, absolute enrichment, by solution, movement, and chemical precipitation. Laterite formation is due to physicochemical interaction between rocks exposed at the surface and infiltrated rainwater which is mainly influenced by rock's mineral composition and their physical properties. Laterite's coloration ranges from brown, red to chocolate with botryoidal or vesicular in structure transforming from Fe-rich uppermost part to clay rich lower part on top of bedrock. Laterite are characterized by high content of Iron (Fe), Aluminium (Al), Zircon (Zr)Manganese (Mn), Nickel (Ni), Copper (Cu), Titanium (Ti), and Vanadium(V) but laterites are also important in exploration of Ni, Au and Cu. Mineral and chemical composition of laterite poses a problem for chemical analysis methods that involve dissolution of the sample. Residual character of the laterite means by its nature that it contains phases that are chemically resistant to weathering and difficult to dissolve completely in typical acid treatments. Therefore, XRF method, devoid of similar problems, is widely applied in laterite studies. However, compositional variation of laterites and strong mineralogical effects make laterite quantitative analysis challenging. In the case of XRF analysis one of the methods in complicated matrices and absence of standards (certified reference materials) is the Fundamental Parameter Method

XRF Fundamental Parameter method (FP) converts instrumental analytical lines to elemental concentrations, accomplished by a calibration step when XRF intensity is measured using a known standard. FP method can be based solely on theoretical equation. Its major advantage includes applicable to many matrices (thin, thick and multilayer specimen), solving non linear equation without normalising at any stage, one standard similar to unknown sample can be used for calibration. The standards are measured then ration of their measured intensities and theoretical intensity is computed using FP package. Modern FP packages are equipped with codes that includes different option such as matching library, theoretical overlap correction, fusion disk correction scatter, charge correction to enhance accuracy. FP method where scatter lines estimate effect of non-analysed components such as ultralight element, the geometry effect which hitherto increases uncertainty in FP method is considered thus while the algorithm computes scatter lines, quantity of sample will not affect analysis accuracy.

The main objective of this thesis is to investigate the application of the Fundamental Parameter (FP) method in XRF to the analysis of major and trace element composition of Fe-rich geological samples, Fe-Al rich lateritic soils and ores using pressed powder pellets.

The goal of this study is to asses the consistency, reliability and accuracy of FP method in different Fe-rich sample matrixes in comparison to standard quantification methods used in XRF analysis.

2. Literature review

2.1 Overview of XRF technique

X-ray fluorescence spectrometry (XRF) is a versatile analytical technique in the qualitative and quantitative elemental analysis of conventional matrices such as geological, cements, and mining sample. [1] Additionally, the instrument's ease of use, speed, precision, and reproducibility extends its application to wide-range other samples such as water & wastewater, catalysts, semi-conductors and lubricants. [2] XRF applicability has extend to polymers and biological materials, archaeological objects, also in the analysis of artworks in recent times. [3] Routinely, elements from Na to U can be determined using Energy-dispersive X-ray Fluorescence (EDXRF) while wavelength-dispersive spectrometers have been proven to allow efficient determination of low proton number (Z) down to Beryllium (Be). Being a non-destructive technique samples can be analysed without treatment but error arising from surface roughness, particle size, sample inhomogeneity can be minimized by powdering and pelletizing with or without binder (ceramics, ores, soils) cleaning and polishing of sample (metals, alloys), fusing with suitable flux (ceramics, ores, rocks) as a means sample preparation for high quality results. [3]

The method principle involves irradiation of sample with a beam of high-energy X-rays. As the excited electrons in the sample fall back to ground state, they emit X-rays that are characteristic of those elements present in the sample. Based on energy or wavelength the X-rays are then filtered and measured via a system of analysing crystals, optics, and detectors. [4] each element has characteristic energy level K or L. This information can be used to identify the elemental composition of the sample. Qualitative analysis requires no form of calibration while quantitative analysis require some form of calibration which either be empirical or based on fundamental parameter approach. [5] Elemental concentration in unknown samples are quantified by comparing the X-ray intensities against known calibration standards. The major merit of XRF over arc or spark emission is its ability to analyse both conducting and non-conducting materials as well as inorganic and organic matrices with minimal sample preparation. [6]

2.2 Quantification Methods in XRF Analysis

Many methods both empirical and theoretical have been put forward for quantitative XRF analysis method selection is mainly depends on sample type (thin or bulk, rock, or alloy), sample preparation methods (fusion, non-treatment) and whether the expected results are semi-

quantitative or quantitative, multi or single element analysis. [3] Rafal *et al*. (2012) broadly classify the quantification methods into compensation and matrix correction methods. Compensation methods exploits the variation in matrix effect due to specimen composition which is like atomic emission or absorption spectrometry thus it requires specific sample preparation (such as internal standard, standard addition, dilution) and only one or few elements can be determined quantitatively. while matrix correction methods became more routinely used due to continuous advances in computation power. Unique feature is that it combines both theoretical calculation and experimental results (empirical or theoretical coefficients).

2.3 XRF quantification using Fundamental Parameter (FP)

Fundamental parameter methods are based upon the mathematical formula Eq. (1) proposed in 1955 by Sherman. The formula is used to calculate the radiation intensity in a specimen of known composition by neglecting tertiary fluorescence hence taking primary and secondary fluorescence into account. This method require that physical constants are known: mass attenuation coefficients, Cöster—Krong transition probabilities, photelectric properties, weight of analytical line within the series, absorption coefficients jump ratios thus these values can be found in the instrumental database (7). Basically, through a calibration step, fundamental parameter method converts element's peak intensities to elemental concentration or film thickness where related parameter ar independent of sample matrix. If the bulk's film thickness is known, then analysis maybe based purely on theoretical equation and fundamental parameter database [7].

$$Ii = \frac{d\Omega}{4\pi sin\phi}\ \mathrm{Q}i\mathrm{q}\mathrm{i}Wi \int_{\lambda min}^{\lambda \mathrm{edge}} \tau i(\lambda) I_{\mathrm{o}}(\lambda) \frac{1-\exp[-X(\lambda,\lambda i)\rho t}{X(\lambda,\lambda i)} \left[1 + \sum_{j} Wj\ Sij\right] d\lambda \qquad (1)$$

Where

$d\Omega$ is the differential solid angle for the characteristic radiation

i,j are the subscript for the analyte and matrix element respectively

Q_i is the sensitivity of the spectrometer for characteristic radiation of analyte i:

W_i, W_j are weight fractions of the analyte *i* and matrix element *j*, respectively;

λ_{min} and λ_{edge} are short wavelength limit and wavelength of analyte absorption edge respectively;

$\tau_i(\lambda)$is the photoelectric absorption coefficient for analyte I and primary radiation of wavelength λ;

$I_0(\lambda)$ is intensity of the primary radiation

$\boldsymbol{\rho}$ is the density of the sample

q_i is the sensitivity of the analyte

S_{ij} is the enhancement of term for matrix element *j* which enhance the analyte *i*

De Boer and Brouwer (1990) described the use of fundamental parameter (FP) software to linearize fundamental parameter algorithms as it depicted non-linear equations- intensity dependence on concentration and layer thickness of each element. Parameter such as tube spectrum, each element's intensities, absorption coefficients, emission wavelength, absorption edges enhances the accuracy of the algorithm. The software is designed to use at least one standard which similar in both concentration and composition to the unknown, using the ratio of experimental intensities to the calculated intensities as a measure of spectral transmission. Given all the instrumental transmission its possible to compute theoretical intensities for an unknown sample which can be compared to measured intensities. (8) FP analysis capability includes single or multiple or standardless calibration scheme if the tube, detector, environmental and geometry parameter are known, it also supports single layer or bulk composition thickness analysis of up to 30 elements calculated as elements or compounds with up to 4 excitation conditions per analysis each defined separately or freely defined with any combination of experimental condition. (9)

2.4 Mineralogical Effect in XRF analysis

Claisse [9] first introduced 'mineralogical effect' concept where he found that two sample of 1% tungsten has three fluorescent intensities of difference of 15%, this was due to variations of mass absorption and particle composition thus when element analysed has many phases whose mass absorption coefficient and resulting X-ray fluorescence radiation varies with the minerals attributed. In wavelength dispersive XRF(WDXRF) spectrometer, analytical line's measured at defined angle and, mineralogical effect causes deviation of lines from theoretical value hence element in a sample tends to exist as a mix of many forms resulting in spectral overlaps, and changes in position (distorted peaks, position, width).

Optimizing the measurement conditions of calibrant, unknown sample, analytical lines, dispersive crystal, operating conditions such as pulse height, peak angle, X-ray tube and background have

proven to introduce additional errors over the years. The best approach for reducing mineralogical effect is to use pressed pellets of unknown and calibrant are of the same composition. [10]

2.5 Matrix Effects in XRF analysis

Matrix effect is caused by absorption or enhancement of radiation in a sample. Intensity of analytical line do not depend on concentration of originating element but other element that makes up the matrix leading to attenuation or enhancement. X-rays pass through layer in the sample to reach the atoms in the sample, this layer absorb incoming radiation also characteristic radiation produced passes through the layers to leave the sample. Absorption depends on energy of radiation, atom's pathlength and sample density. When matrix elements emit characteristic radiation of energy above that of analyte's absorption edge, thus excited analyte emitting additional characteristic radiation directly from the X-ray source. This is known as secondary fluorescence or enhancement. [11] Fundamental parameter matrix correction model is very robust, if the major matrix is known the model can be used on a full concentration range on all types of samples. based on Sherman's equation which describes element's intensity - sample composition relationship requiring few calibration standards. [11]

2.6 Laterites

2.6.1 Historical Background

The cardinal features for deriving the basis for defining laterite are; -

- Iron, aluminium, manganese oxides and titanium's presence in large quantity of varying proportions
- Depletion of free silica(quartz)
- Large percentage of aluminium than necessary to combine with free silica to form Kaolinite.
- Negligible amounts or no bases and alkalis
- Hardening on exposure to air

Laterites is used a term for petrographic term for rock, generally cavernous and vesicular, rich in hydrated iron and aluminium oxides and depleted bases of aluminium. (12)

Laterite are well known in Africa and Asia as building material. (12) Until 20^{th} century laterite was perceived as a rock, but today, Laterite is classified as iron precipitate where accumulated

material could be remobilized under different condition thus affecting its concentration. (13) These redistribution and re-precipitation of iron known as absolute iron accumulation occur due to upward migration from deep layers and downward from overlying soil which is concentrated in deeper 'illuvial horizons'' similarly ground water's lateral migration within fluctuating zone from higher landscape. [12]

2.6.2 Modes of formation of laterite

Formation of laterite is termed laterization, it describes the process of addition of iron due to movement of dissolved ferrous with oxidation – precipitation producing an Fe-rich laterite. The advances on laterites research over the years depicts in situ weathering mechanism in laterite formation from diverse parentage and aggregation in resultant residuum. Reaggregation defines degree of maturity. Tropical weathering (Laterization) occur due to prolonged process of chemical weathering thus producing wide range in the thickness, chemistry, grade and minerology of resulting soil. [14] The dominant process of laterite formation is the residual enrichment of Fe-Al with removal of Silica, Alkaline and Alkaline earths. In a bid to further understand its formation in given soil or landscape, Abd.Rashid[13] introduced a systematic approach: - the source of Fe moving, how its mobilized, how its precipitate and how the hardening process occurs leading to understanding the formation of laterites. Weathering of rock due to intensive rainfall and extreme temperatures causing a chemical reaction between rocks exposed and infiltrated rain water. Mineral composition of rock and their physical properties controls this reaction. Another relevant factor in laterite formation is the property of reacting water such as temperature, dissolved constituents, acidity, pH, redox potential. Chemical weathering is slower in tropical and subtropical region due to prolonged dry season and high annual precipitation. [12]

Mineralogical and chemical research shows that primary minerals are not fully dissolved but partially transforms in secondary minerals which are more stable under intensive weathering conditions, Na, K, Mg, and Ca don't react with other element hence are removed by percolating water. Lower pH of water causes initial dissolution which removes high percentage of dissolved Silica(Si) but some portion of Si react with dissolved Aluminium(Al) to form clay mineral Kaolinite. Gibbsite ($Al(OH)_3$ is formed when dissolved Si concentration is low, this chemical alteration corresponds mineralogically with the formation of Gibbsite and Goethite FeOOH. Fe

being very reactive with hydroxyl ions forming after oxidation of Goethite and Hematite resulting in red-brown colour of laterites. [12]

2.7 XRF Sample preparation methods

X-ray fluorescence is frequently used in cement, iron, silicate rocks as quality control tool in a manufacturing process, monitor for product quality and geochemical characterization, fusion or pressed pellets are used based on purpose of analysis. [16] Fusion method entails the use of alkali borate flux to fuse samples at high temperature to make a glass bead, though meaningful homogeneity and accuracy are ensured, it's time consuming - expensive technique. The pressed powder pellets method requiring no chemical processes, sample is pulverized to ensure homogenization then pressed using pressing machine into a cup or ring. This method is suited for rapid analysis of bulk samples. Grain size, mineralogical heterogeneity effect are common matrix effects of this method thus a robust sample preparation and powder pattern/characterization is required to eliminate errors arising from these effects.

2.8 Method validation

Method validation is a process of confirmation by examination and provision that the specific requirement for intended use are fulfilled. Based on international best practices, method validation is a requirement in analytical laboratories to demonstrate its qualification and competence. ISO 17025:2006 emphasise that: Laboratories shall validate standard methods, in-house methods, in a manner that amplification and modification of standard method to confirm that the method are fit for its intended use.'' The laboratory should demons its ability that will earn Client's trust this involve giving analytical answer to questions raised by clients hence results obtained have verifiable' 'fitness-for-purpose''. [17-18] Good analytical result relies on unequivocal specification of analytical requirement which reflects minimum fitness-for-purpose criteria that the method must meet towards solving a problem. The extent of validation and performance parameter to be evaluated/characterized depends on status and experience of the method. It implies studies to determine method performance parameters are carried out using equipment within method's specification and optimized appropriately. [17-18]

2.9 Validation parameters

2.9.1 Selectivity

Establishing that the signal produces by the instrument was due to the analyte not any other inferring components. Selectivity characterizes instrument's reliability in presence of interferences [17] WDXRF analytical method has capability of scanning the analyte which afford analyst to identify and deselect interfering elemental lines (Kα, Lα)hence optimizing the instrument to be selective to analyte while calibrating for quantitative analysis.

2.9.2 Scope of application, Linear range. Limit of detection, Limit of quantitation

In any quantitative methods, stating the range in which the method is applicable in terms of concentration, limit of detection and limit of quantification imposed based on instruments system. In validation, its vital to indicate the level at which detection is not reliable. The instrumental limit of detection is the concentration at which the instrument can detect with certain reliability while if limit of quantitation is the concentration that can be quantitatively expressed with certain reliability. [17] FP method is based on correlation of theoretical intensity and measured intensity using the regression for linearity check before developing a calibration plot for the analyte. Since the varying analyte concentration is not in the scope of the method, instrument's linear range, limit of detection will be evaluated.

2.9.3 Accuracy (trueness and precision)

Studies of trueness and precision of an analytical method are key validation criteria, it's critical part of measurement uncertainty. method validation evaluates accuracy of a results by estimating both systematic and random error effects on results. trueness asserts the closeness between mean set of results to the true value, likewise it indicates method applicability with real samples. Bias estimate is used to express trueness, using mean and standard deviation results from a method, and comparing with known values of certified reference material. The ideal reference material is a certified material should be closely similar in terms of matrix to analyte of interest. Precision is a measure of result's closeness to one another, it's usually expressed as standard deviation. The two common precision measures are reproducibility and repeatability, they describe the two-extreme measure of precision. Repeatability is an interpretation of variation to anticipate when a method is performed in replicate by an analyst on a given equipment over a brief timescale. When a sample is analysed by two or more laboratories for interlaboratory comparison, largest expected precision used hence reproducibility. This type of precision can be used in a single laboratory (sometimes referred to as intermediate precision) but the exact condition must be stated. [17-19]

2.9.4 Measurement uncertainty

Measurement uncertainty afford the laboratory to know the quality of their measurement result for improvement and conformity. It's also required by Standard ISO/IEC 17025. Measurement uncertainty is a single parameter defining the range of values possible based on the measurement result expressed as standard deviation or confidence interval. Statistical-measurement approach is the basis for its evaluation where different uncertainty sources are estimated and combined into a single uncertainty estimate. There are two main approaches to measurement uncertainty viz single laboratory and interlaboratory approach. Interlaboratory can be either proficiency Testing (between Lab Variability using different procedure based on ISO guide 43, ISO 13528) or interlaboratory validation (same procedure reproducibility and bias based on ISO 5725, ISO TS 21748) while single laboratory approach can be model based using ISO GUM evaluation or single lab validation (Within-Lab reproducibility& Bias Nordtest TR 537).

The Nordtest validation approach involves estimating reproducibility within the laboratory(**Rw)** from control samples or other estimates and estimation of method &laboratory Bias (**ubias**) from Certified Reference Material, Proficiency Test or Recovery test. Combined standard uncertainty u_c is estimated as root sum of squares of the two components expressed as % relative uncertainty. (20)

$$\mathrm{uc}\,\% = \sqrt{\%\mathrm{Rw}^2 + \%\mathrm{ubias}^2} \qquad \textbf{(2)}$$

3 Material and Methods

3.1 Origins sampöes and Geology of Sampling Locations

The lateritic geological samples used for this analysis were collected from three different locations with distinct climatic and geological background: -

-French Guiana which is characterised by old south American terranes compound of diorites-gabbros and granite various degrees of metamorphism, early to late Precambrian age.

- Bosumtwi meteorite impact crater in Ghana. The impact target rocks were phyllites, graywackes, and quartzites and Brimian metamorphosed basalt and pyroclastic rocks.

- crystalline basement north Estonia that is composed of intensely folded deeply metamorphosed and magmatized stratified metasedimentary and volcanic suites.

3.2 Geological description of lateritic samples

3.2.1 B20G – strongly weathered glass-rich impact breccia - Bosumtwi crater, Ghana

The Bosumtwi impact structure is a 10.5-km in diameter complex impact crater in Ghana, West-Africa. Having formed about 1.07 milliom years ago, it is a relatively young and well-preserved structure. The steep inner rim rising about 250-300 m above the surrounding relief is surrounded by a minor irregular circular depression which is in turn surrounded by an outer ring with minor topographic heights and a diameter of about 20 km.Sample B20 is form the norther rim of the crater at Sarpong Nkwanta locality. Mineralogically it is composed of kaolinite about 75%, quartz 10%, cristobalite and plagioclase about 10%, and semiamorphous Fe-Al oxyhydroxides.

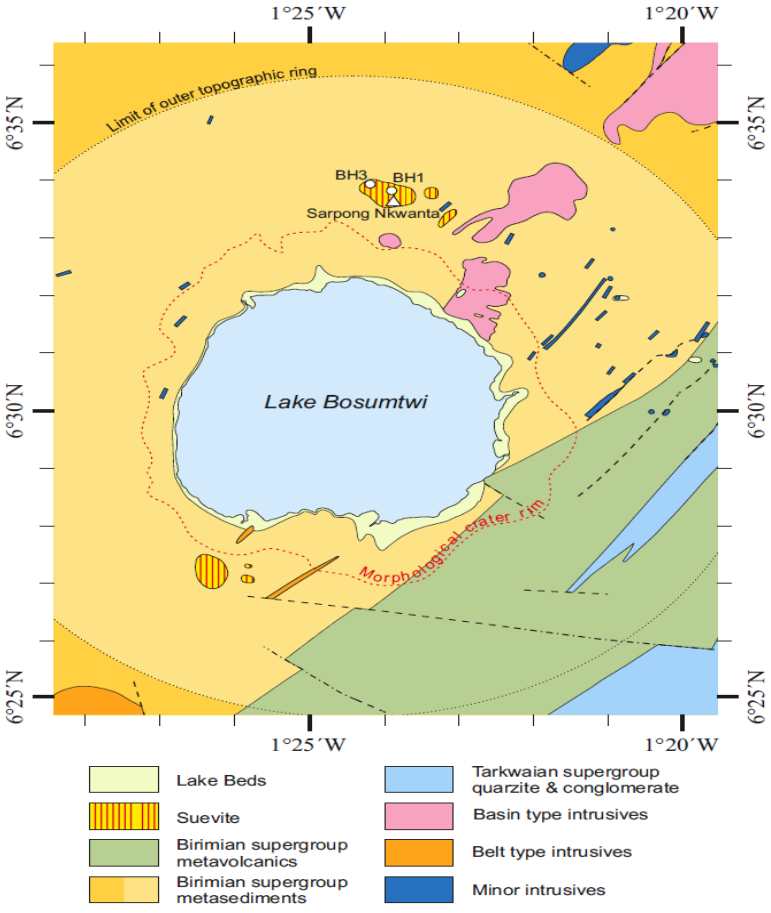


Fig 1 thematic map of Lake Bosunmtwi, Ghana

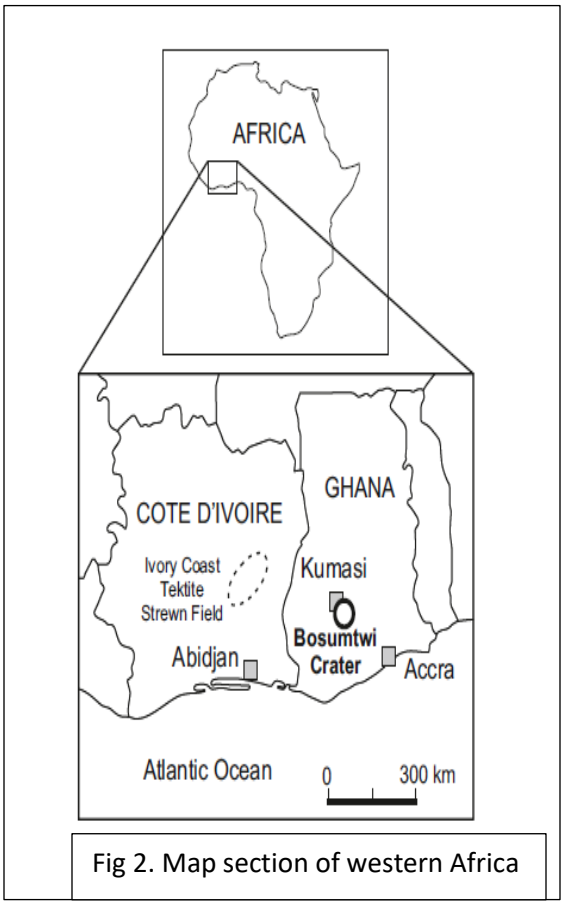


Fig 2. Map section of western Africa

3.2.2 KAW -014 – lateritic weathering crust, French Guyana South-America

Strongly weathered lateritic Fe-rich weathering crust with strong secondary Fe-mineral impregnation. Weathering crust has an age from late Mesozoic to Recent and is composed of gibbsite 60%, hematite-goethite 38 % and anatase ca 1-2 %

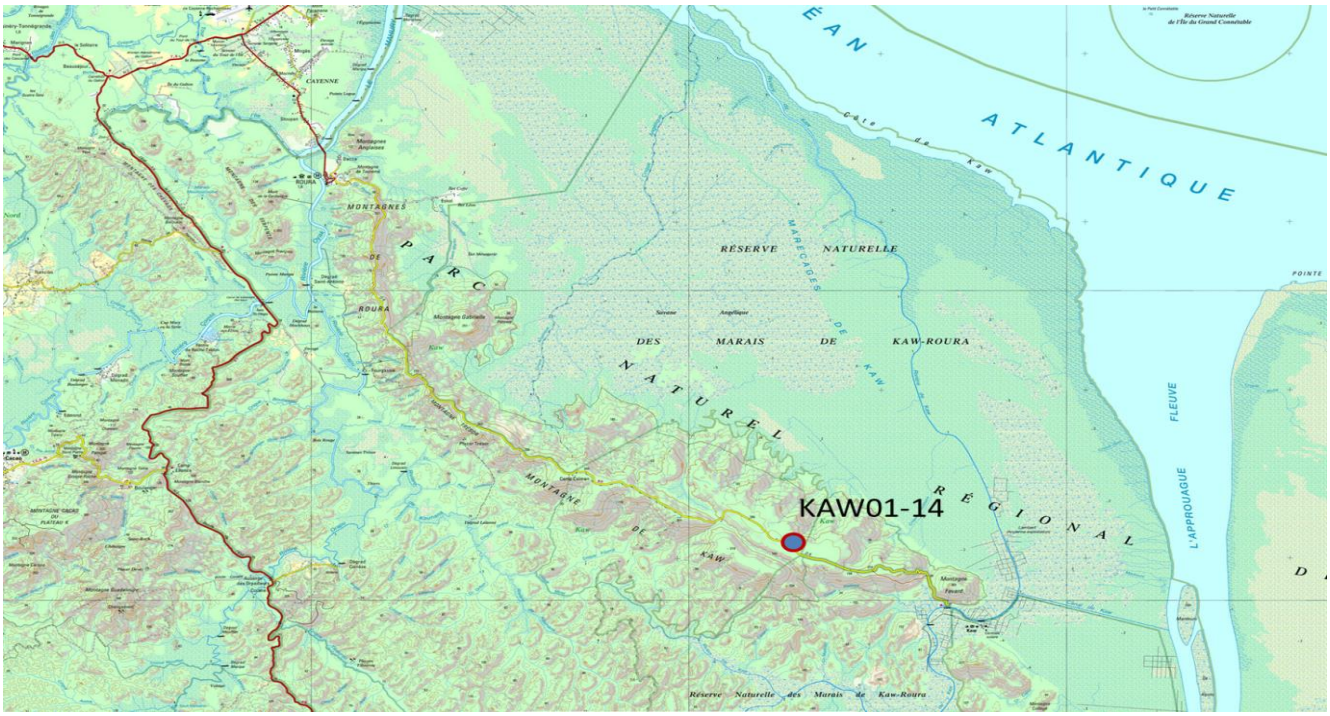


Fig. 3 A map displaying the location of sampling location in French Guyana

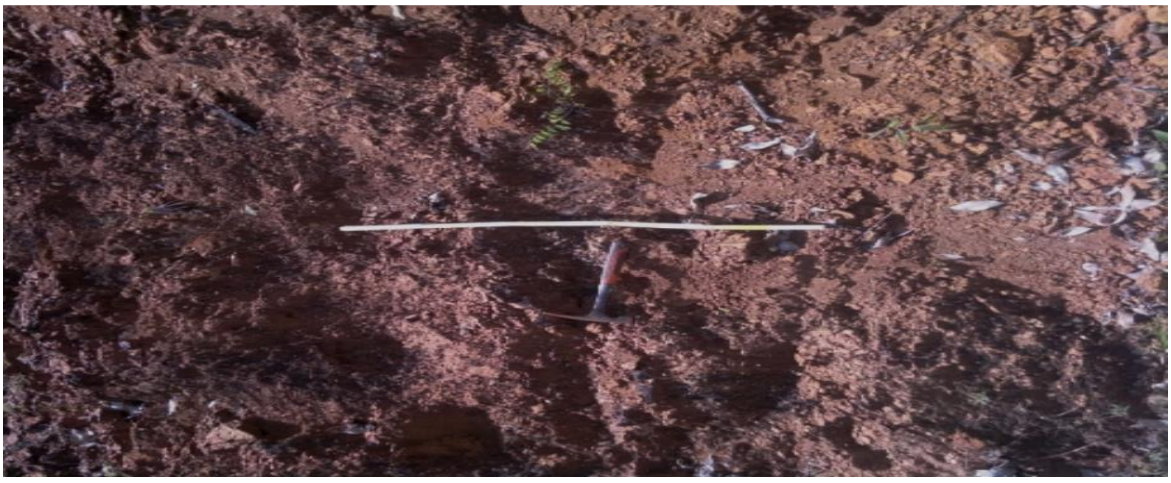


Fig.4 photograph of the sampling site in French Guiana

3.2.3 Paleoweathering crust in drillcore F231 at the depth of 269.4 m

This is from a Baltic Paleosol, Neoproterozoic lateritic weathering crust with an age of 560-600 million years. Sample is from the uppermost part of the weathering crust and is taken from the F231 drillcore depth of 269.4 m. This weathering crust is not exposed on the ground surface but is found below the Ediacran-Paleozoic deposits on the top of the altered crystalline basement. Mineral composition of the sample is dominated by quartz 31%, kaolinite 33%, hematite and goethite 10-12% and illitic mineral about 10%, and K-feldspar 5%. Drill core is located in Uhtna northern Estonia next to Uljaste village

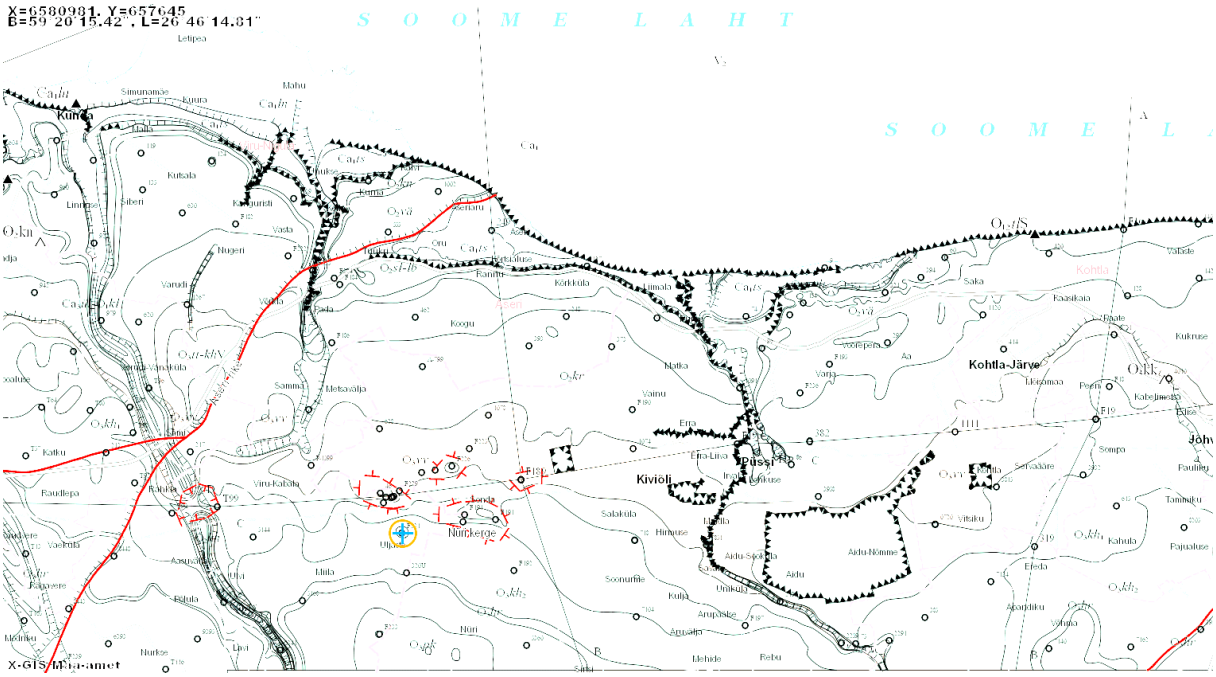


Fig. 5 Geological map of northern Estonia

4 Experimental

4.1 Sample preparation

Each of the lateritic sample were pulverized using a Fritsch vibratory **pulvessete 6** mill to a grain size of about 300-400 microns in the first step using large steel and/or WC balls (diameter 10mm). The samples tend to cake after pulverizing, so mortal & pestle were used to enhance homogenization. In the next step with 5mm balls the final products were achieved - fine grained (< 10_µm) powder. sample were placed in a crucible and dried in an oven for 24 hours at 105°C. followed by drying in muffle furnace at 950°C to obtain LOI data, after drying 5.00 grams of each sample were pressed into pellets into Aluminum cups of 40mm thickness and 27mm diameter using Herzog TP 20 P mechanical press at 100kN force.

The pressed pellets are then place in a sample holder, then placed in Rigaku ZSX Primus II optimized to run at EZ-scan mode using SQX Scattering FP method for qualitative analysis and semi-quantitative scanning of the samples to obtain their matrix composition, detection limit, interfering element, peak overlaps from instrument common library of coefficients. Mineralogical characterization, a portion of powder samples is taken for X-ray diffraction analysis to obtain their crystalline pattern structure from ICDD database. These two analyses serve as a guide for selection of suitable reference materials for calibration.

4.2 Preparations of CRMs and Sample for quantification

Different Certified Reference materials (CRM) used are **190a,1V,386a,3V,56a,25V** and **56b**. they were selected based on the mineralogical information from the qualitative and semiquantitative XRF and XRD analysis, CRMs selected comprises of Flint clay ($Al_2O_3.2SiO_2.2H_2O$), Silicate rock (Cristobalite SiO_2, Bauxite (Gibbsite $Al(OH)_2$, Boehmite ($AlO(OH)$), Goethite($Fe(OH)_3$, Iron ore, Titanium-magnetite ore. The CRMs were dried at 105°C for 24 hours. They were homogenized in a mortar then pressed using 100kN force into Al cups of 27mm diameter. Both CRMs and samples were prepared in replicates.

4.3 Instrumental optimization

Rigaku ZSX Primus II WDXRF spectrometer is used for this work, its possess a 3kW rhodium target X-ray tube with a 3kW, 60kV-100mA generator. The instrument is equipped with ten automated crystal changer mechanism, four position diaphragm-primary beam filter(collimator), 30mm measuring diameter and a Scintillation and Gas flow proportional counter detector. LiF

(200), PET and RX25 analyzing crystal enhance its capability to analyze low Z elements. Hardware configuration makes the instrument simplifies routine maintenance and cleaning. The tube above optics geometry greatly optimized powder sample analysis thus prevents contamination of magnetic valves, vacuum system in the spectrometer chamber. Its spectral design for sample positioning reduces analytical errors arising from sample height and distance variation. The software can operate at different modes such as EZ scan for qualitative analysis, semi- quantitative analysis of sample then quantified them using SQX program which runs standardless FP method. Other feature are drift correction, reference standard samples fixed angle analysis, theoretical overlap correction, as well as sample matrix effect correction. Detailed analytical condition for each element is depicted in table 1.

Table -1. Instrumental parameters for determining major and trace in lateritic soils by WDXRF using 4kW end window Rh tube and PHA* range of 100-300

Element	Analytical conditions									
X-ray line	2Ɵ			Count time (sec)			Silt	Crystal	Detector[a]	kV-mA
	Peak	**Bg1**	**Bg 2**	**Peak**	**Bg1**	**Bg 2**				
Si-Kα	109.000	106..550	111.550	40	20	20	S4	PET	PC	50-60
Ti-Kα	86.100	85.510	86.710	20	10	10	S2	LiF1	SC	50-60
Al-Kα	144.610	143.100	147.200	40	20	20	S2	PET	PC	50-60
Fe-Kα	57.500	56.900	58.100	20	10	10	S4	LiF1	SC	50-60
Ca-Kα	113.130	110.124	111.124	10	20	20	S4	LiF1	PC	40-75
Mg-Kα	36.900	36.250	40.950	40	20	20	S4	RX25	PC	30-100
Mn-Kα	62.950	62.350	63.550	10	10	10	S2	LiF1	SC	50-60
P-Kα	141.190	139.180	142.180	10	20	20	S4	Ge	PC	30-100
K-Kα	136.680	134.180	139.180	40	20	20	S4	LiF1	PC	50-60
Na-Kα	47.250	45.250	49.250	40	20	20	S4	RX25	PC	30-60
S-Kα	110.700	108.220	112.820	10	20	20	S4	Ge	PC	50-100
F-Kα	75.910	73.410	78.410	40	20	20	S4	RX25	PC	30-100
Cl-Kα	92.880	90.870	94.874	10	20	20	S2	Ge	PC	30-100
V-Kα	75.910	76.304	77.504	10	10	10	S2	LiF1	SC	50-60
Cr-Kα	69.330	68.730	69.930	10	10	10	S2	LiF1	SC	50-60

Co-Kα	52.770	52.374			10	10	S2	LiF1	SC	50-60
Ni-Kα	48.650	48.044	49.244	10	10	10	S2	LiF1	SC	50-60
Cu-Kα	45.040	44.410	45.610	10	10	10	S2	LiF1	SC	50-60
Zn-Kα	41.780	41.180	42.380	10	10	10	S2	LiF1	SC	50-60
Ga-Kα	38.900	38.300	39.500	10	10	10	S2	LiF1	SC	50-60
Ge-Kα	36.310	35.714	36.914	10	10	10	S2	LiF1	SC	50-60
As-Kα	33.980	33.380	34.500	10	10	10	S2	LiF1	SC	50-60
Se-Kα	31.870	31.270	32.470	10	10	10	S2	LiF1	SC	50-60
Br-Kα	29.950	29.350	30.550	10	10	10	S2	LiF1	SC	50-60
Rb-Kα	26.600	26.00	27.200	10	10	10	S2	LiF1	SC	50-60
Sr-Kα	25.130	25.534	25.534	10	10	10	S2	LiF1	SC	50-60
Y-Kα	23.780	23.184	24.384	10	10	10	S2	LiF1	SC	50-60
Zr-Kα	20.390	19.450	20.600	10	10	10	S2	LiF1	SC	50-60
Nb-Kα	21.390	20.700	21.924	10	10	10	S2	LiF1	SC	50-60
Mo-Kα	20.320	19.720	20.920	10	10	10	S2	LiF1	SC	50-60
Sn-Kα	14.030	14.630			10	10	S2	LiF1	SC	50-60
Sb- Kα	13.450	12.850			10	10	S2	LiF1	SC	50-60
Te- Kα	12.900	12.304	13.504	10	10	10	S2	LiF1	SC	50-60
Ba-Lα	87.130	87.374			10	10	S2	LiF1	SC	50-60
Ta-Lα	44.400	43.794	44.994	10	10	10	S2	LiF1	SC	50-60
Pb-Lβ1	28.240	27.640	28.840	10	10	10	S2	LiF1	SC	50-60
Bi- Lα	32.990	32.390	33.590	10	10	10	S2	LiF1	SC	50-60

[a] PC = Proportional Counter, SC = Scintillation counter, PHA- Pulse Height Analyzer

4.4 FP Quantitative analysis

FP method expresses x-ray intensity as a function of chemical composition, physical constants, and sensitivity of an analyte. FP quantification is done by regression of theoretical intensity and measured intensity. Since intensity of any sample is proportional to concentration, modified by both absorption and enhancement effects which is a function of sample composition and primary spectrum from the x-ray tube. To remove these effect, a calibration plot is developed that will eradicate these effects. In this FP method, CRMs were measured using the instrumental conditions in table 1, the plot of their measured intensity against theoretical intensity is used to develop a calibration curve for the unknown samples. The major and trace elements analytical conditions, as displayed in table 1, calibration plot using CRMs major element (figure 1) are simple, linear with low residual between the measured intensity and theoretical intensity. Matrix effect and co-existing element were computed by the ZSX software, capable of autocorrection program that calculate α – coefficients based on best matrix matched algorithm with CRM composition, both the major and trace components of the lateritic samples were targeted in this application but only the major element were considered in selecting the CRMs to be used in calibrating. Replicate measurements

were made to evaluate repeatability. calibration plot (figure 1) were developed from the CRMs result which was used to quantify the unknown samples. The samples were then measured and quantified based on the calibration plot developed from CRMs.

5 RESULTS AND DISCUSSION

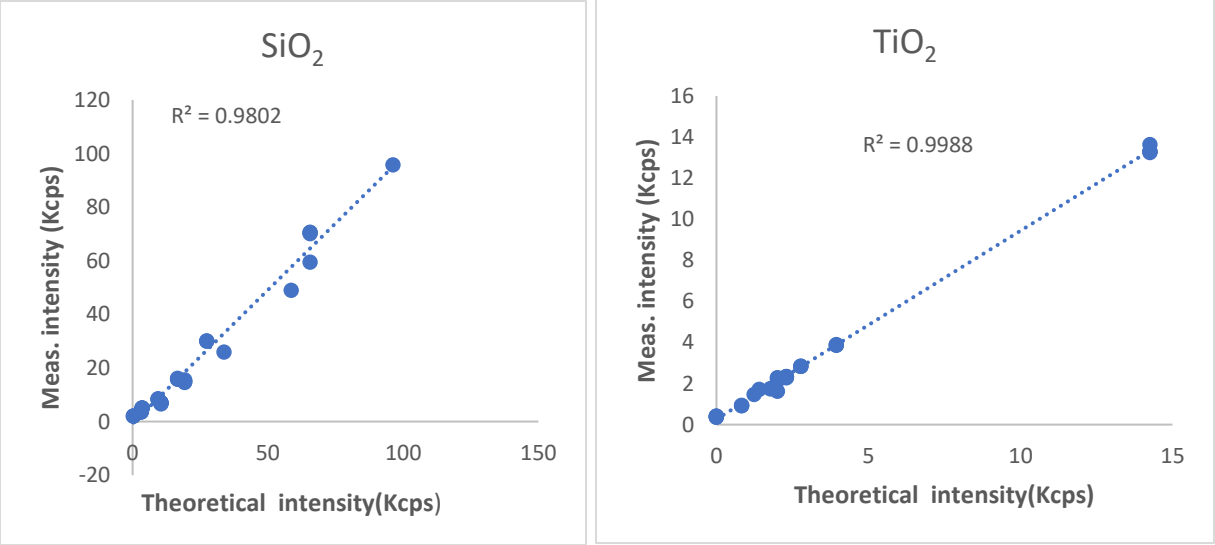
5.1 Linearity

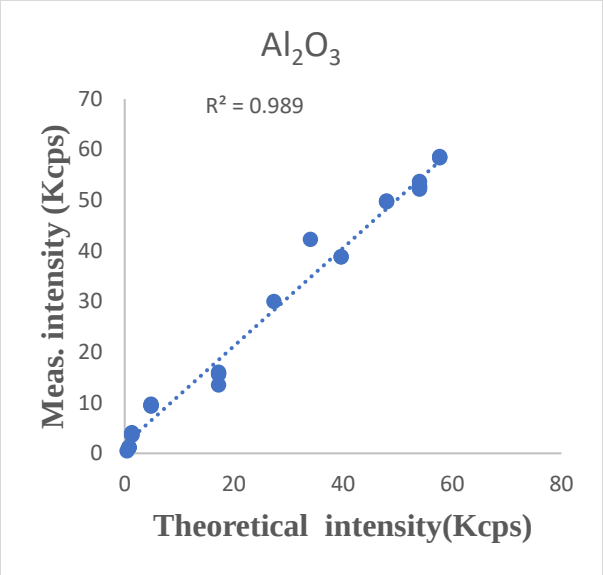
Table 2 and figure 1 depicts the linearity result. Correlation coefficient of all the components of the CRMS for the calibration were within linear range and there is a positive correlation between the theoretical and measured intensities. Element overlap had earlier been corrected by setting the analytical condition for each element's measurement. matrix effect was corrected using theoretical alpha coefficient taking Loss on ignition into account.

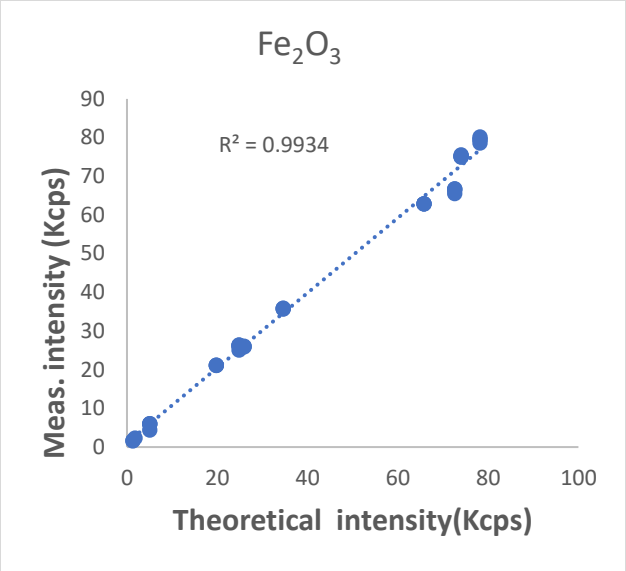
Table 2 Result of linearity

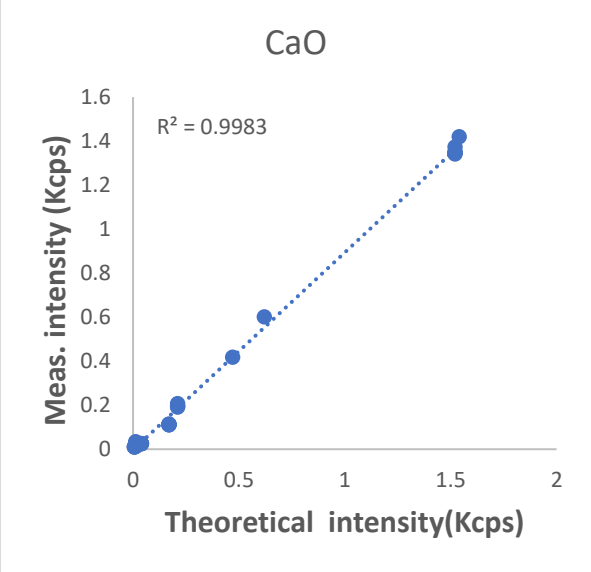
Components	SiO2	TiO2	Al2O3	Fe2O3	CaO	MgO	MnO	P2O5
r of calibration curve	0.9907	0.999	0.995	0.999	0.998	0.998	0.998	0.995
R^2 between calibration curve and FP method	0.9802	0.9996	0.989	0.9934	0.9983	0.9942	0.9977	0.9935

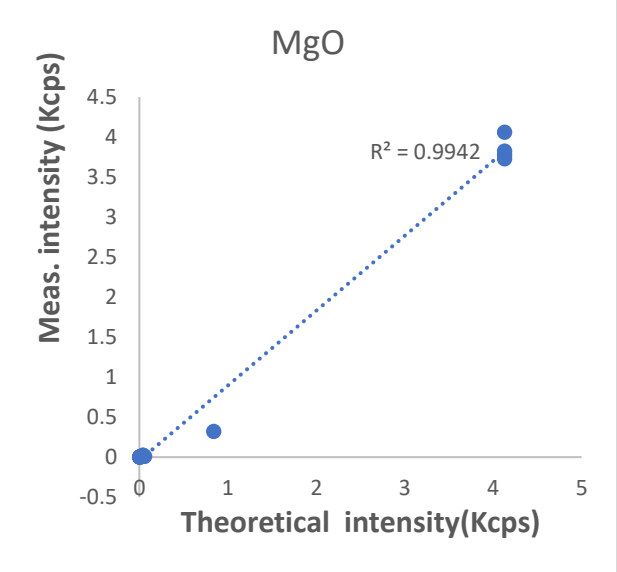
Figure 1 Calibration plots of 7 analysed CRMS components using FP method

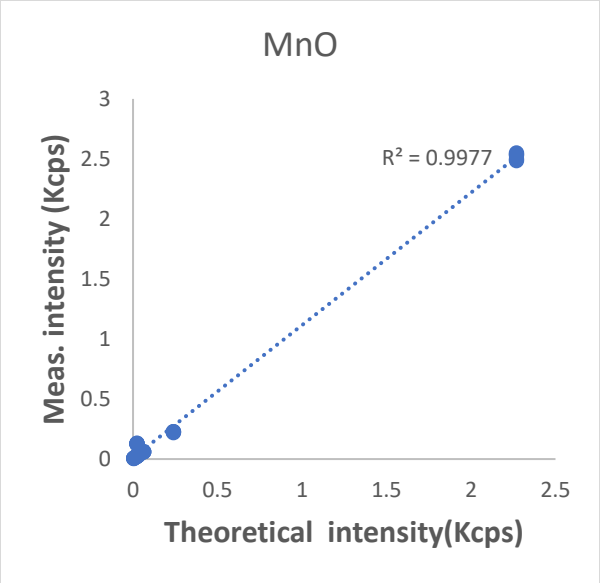


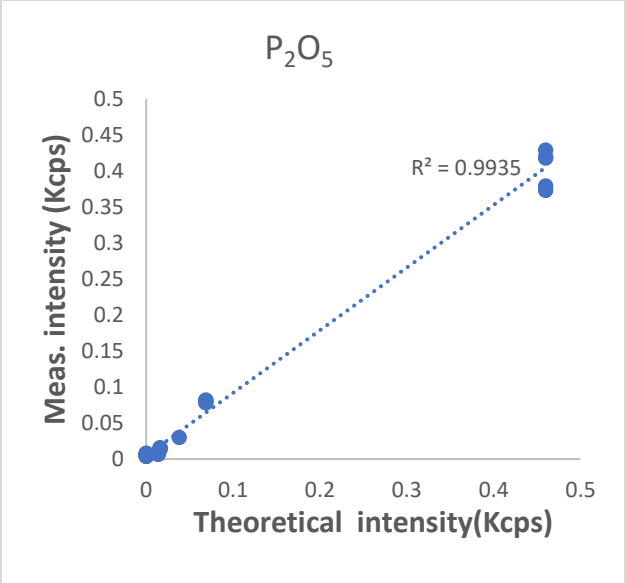

Al_2O_3
R² = 0.989
Meas. intensity (Kcps)
Theoretical intensity(Kcps)
0
10
20
30
40
50
60
70
0
20
40
60
80


Fe_2O_3
R² = 0.9934
Meas. intensity (Kcps)
Theoretical intensity(Kcps)
0
10
20
30
40
50
60
70
80
90
0
20
40
60
80
100


CaO
R² = 0.9983
Meas. intensity (Kcps)
Theoretical intensity(Kcps)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
0.5
1
1.5
2


MgO
R² = 0.9942
Meas. intensity (Kcps)
Theoretical intensity(Kcps)
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
1
2
3
4
5





5.2 Accuracy

5.2.1 Specificity

The accuracy of this method is based on the standard error evaluation between the CRMs consensus values and the FP method measured values, (21) which were found to be within acceptable criteria for FP method as the sample are usually in bulk or in a batch of industrial process. Calibration curve accuracy was evaluated using linest function. The results were displayed in table 3.

Table 3. Calibration curve and Calculated standard error estimate

components	calibration Range	Accuracy of calibration	Standard Error (σ_est)
SiO_2	0.27 - 96.2	± 0.029	1.75
TiO_2	0.11 - 14.26	± 0.004	2.61
Al_2O_3	0.42 - 62.3	± 0.023	2.31
Fe_2O_3	78.21 - 1.31	± 0.021	0.89
CaO	0.04 - 1.54	± 0.008	0.02
MgO	0.06 - 4.13	± 0.019	0.49
MnO	0.033 - 2.27	± 0.012	0.19
P_2O_5	0.016 - 0.46	± 0.019	0.007

5.3 Method's Performance Characteristics

To demonstrate that that FP method used is Fit-for-Purpose, the method must be evaluated using Single Laboratory Validation approach (NordTest Tr537). It involves calculating the uncertainty of the whole method which considers systematic error and random error to assess trueness and precision evaluated using **Laboratory Bias** and **Repeatability/Reproducibility,** root sum of squares of these two component gives combined standard uncertainties $\mathbf{u_c}$ express as % relative uncertainty.

5.3.1 Trueness

The trueness is estimated as bias which the percentage of mean measured CRMs in replicates(n-8) using FP method from the consensus CRMs values. The 7 CRMs bias was evaluated, th their root mean square **($\mathbf{RMS_{bias}}$)** to avoid underestimation, its account for average bias of the FP method then average uncertainty of the CRMs values as shown in equation 3-6 below. [20]

$$\mathbf{Bias} = \mathbf{Clab} - \mathbf{Cref} \qquad (\mathbf{3})$$

$$\mathbf{u(Cref)} = \frac{\sqrt{\mathbf{u(Cref)^2}}}{\boldsymbol{n}} \qquad (\mathbf{4})$$

$$\mathbf{RMSbias} = \frac{\sqrt{\boldsymbol{\varepsilon}\mathbf{bias^2}}}{\boldsymbol{n}} \qquad \mathbf{(5)}$$

$$\mathbf{u(bias)} = \sqrt{\mathbf{RMSbias^2} + \mathbf{u(Cref)^2}} \qquad \mathbf{(6)}$$

Where Clab = Laboratory result

Cref = CRM value (consensus value from Certificate)

u(Cref) = uncertainty values of CRMs

RMS_{bias}= Root Mean Square of Bias

5.3.2 Precision

The precision of the instrument was computed by 10 replicate analysis of CRMs, was calculated using the within lab reproducibility (long time repetition) standard deviations (**Rw**, n=10), their combined uncertainty **uRw** was calculated by root sum square of their **Rw,** all CRMs reproducibility values were less than their respective combined standard uncertainty except for CaO and P_2O_5 where the two values were the same.

The sample precision was estimated using their pooled repeatability of replicate sample measurements (n=20). Repeatability was evaluated by running replicate measurements in different days under the same condition and taking their respective standard deviations while Reproducibility was evaluated for CRMs, hence taking respective standard deviation of replicate measurement on different days. It should be noted in table 5 (A-E) that the precision of samples and their repeatability were almost the same due to stability of Rh-tube, detector, and goniometer of the instrument. The variation was due to sample preparation owing to heterogeneity of sample component, in KAW-014 B, KAW-014 C and B20G all have noticeable variation in their component SiO_2, TiO_2 Al_2O_3, Fe_2O_3 this can be improved by using geo-specifics CRMs. E_n values are also estimated to measure consistency of FP method value to the CRM consensus values. The En values for all the CRMs major component were satisfactory ($E_n < 1$) this further indicate that FP method is Fit-for-Purpose.

5.4 Measurement uncertainty

Replicate measurement standard deviation of CRMs analyses prepared on different days account for random effect as an intermediate precision and the values u(**Rw**) were obtained as depicted in table 4. The values were below 0.2% (except P_2O_5) for samples analysed. This same value was used to determine bias (systemic error). Calculated RMS_{bias} from the FP method gave relative bias range of 0.01 - 0.2 % for the 7 CRM's components. The combine uncertainties uc reveals that values were below 0.25%, using coverage factor of k =2, the relative expanded uncertainty was in the range of 0.1 – 2.1%.

Table 4. Validation Parameter

CRMs components	u(Bias) (%)	SRW (within -Lab) (Mass%)	Combined uncertainty u_c	U (k=2,Norm)	E_n score
SiO_2	0.2	0.07	0.31	0.6	-2.3
TiO_2	0.1	0.12	0.22	0.4	-4.9
Al_2O_3	0.6	0.10	0.69	1.3	0.5
Fe_2O_3	1.0	0.04	1.03	2.1	-0.2
CaO	0.02	0.05	0.05	0.1	-4.8
MgO	0.1	0.14	0.21	0.4	-0.6
MnO	0.01	0.06	0.06	0.1	-2.5
P_2O_5	0.02	0.23	0.23	0.1	-0.1

.

Table 5 A-E precision and repeatability data of sample analysed

Table A sample B20G

B20G (Mass%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3
X(n=20)	45.811	0.912	32.250	11.049	0.212	0.138	0.057	0.048	0.113	0.065	0.020
RSD	0.02	0.06	0.02	0.04	0.11	0.16	0.11	0.06	0.73	0.13	1.37
Precision	1.10	0.06	0.80	0.43	0.02	0.02	0.01	0.003	0.08	0.01	0.03
Repeatability	0.352	0.006	0.157	0.203	0.003	0.001	0.002	0.001	0.005	0.005	0.015

Table B sample F231-A

F231-A (Mass%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3
X(n=20)	37.399	0.738	35.116	18.034	0.095	0.179	0.014	0.035	2.348	0.061	0.015
RSD	0.04	0.09	0.02	0.05	0.07	0.17	0.07	0.06	0.07	0.18	0.59
Precision	1.52	0.07	0.54	0.89	0.01	0.03	0.001	0.002	0.16	0.01	0.01
Repeatability	0.263	0.009	0.205	0.109	0.005	0.015	-	0.001	0.076	0.005	0.006

Table C sample KAW 014 B

KAW 014B (Mass%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3
X(n=20)	1.672	2.064	49.239	20.427	0.004	0.000	0.002	0.082	0.066	0.001	0.053
RSD	0.36	0.02	0.02	0.06	0.45	-	0.37	0.03	0.70	0.58	1.10
Precision	0.59	0.04	1.15	1.13	0.002	-	0.001	0.003	0.05	0.001	0.06
Repeatability	0.069	0.025	0.721	0.002	-	0.001	0.001	0.002	0.002	0.001	0.035

Table D sample KAW 014 C

KAW 014C (Mass%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3
X(n=20)	1.696	1.616	35.323	42.406	0.015	0.000	0.000	0.060	0.013	0.006	0.101
RSD	0.23	0.23	0.24	0.24	0.23	-	-	0.24	0.77	0.61	1.20
Precision	0.07	0.02	2.49	2.39	0.002	-	-	0.003	0.01	0.004	0.12
Repeatability	0.037	0.007	0.902	0.809	0.001	-	-	0.001	0.001	0.002	0.063

Ta ble E sample KAW 014D

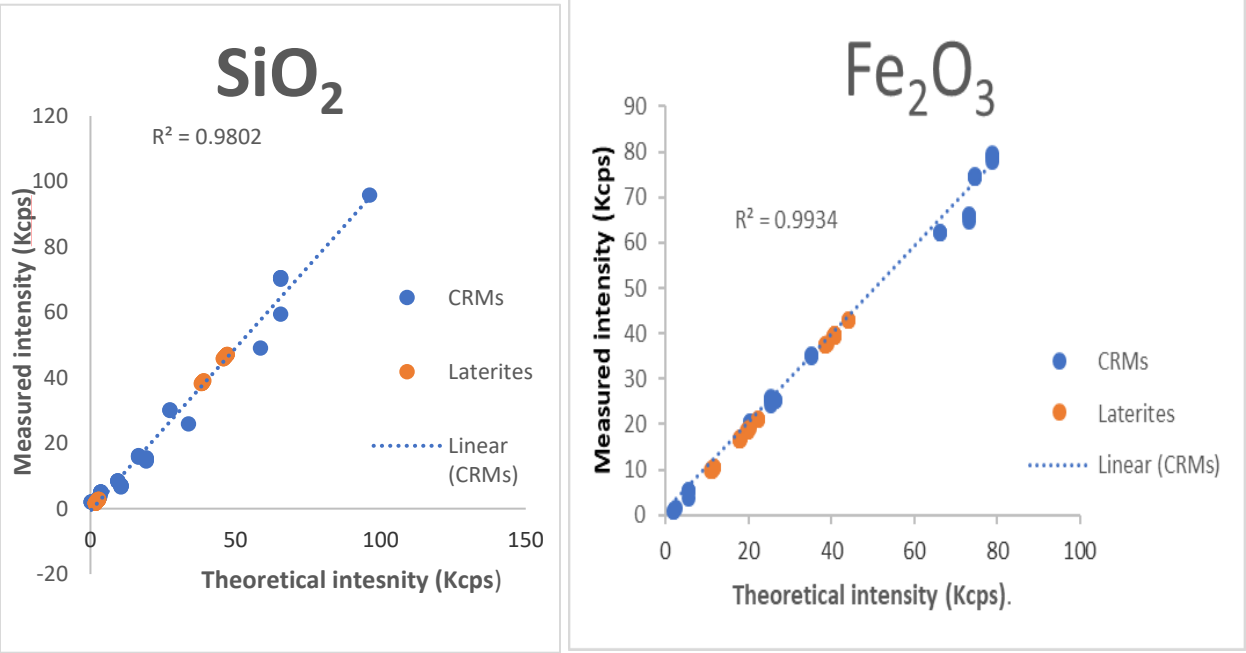
KAW 014D (Mass%)	SiO2	TiO2	Al2O3	Fe2O3	CaO	MgO	MnO	P2O5	K2O	Na2O	SO3
X(n=20)	2.722	2.757	36.533	38.705	0.036	0.000	0.004	0.050	0.032	0.004	0.115
RSD	0.02	0.01	0.03	0.03	0.07	-	0.12	0.05	0.06	0.52	0.96
Precision	0.06	0.02	1.14	0.91	0.00	-	0.001	0.003	0.002	0.002	0.15
Repeatability	0.038	0.016	0.820	0.652	0.003	.	-	0.002	0.002	0.002	0.100

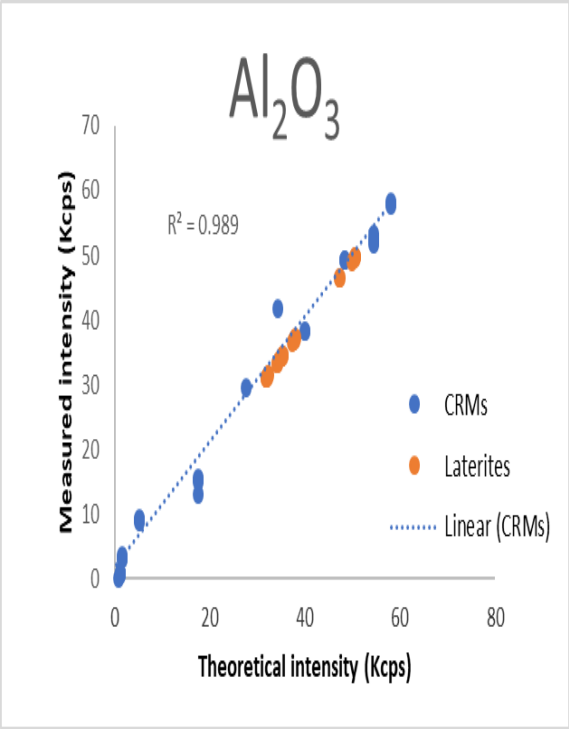
5.5 Discussion

The specificity of the FP method was scrutinized by checking each element spectrum in the CRM and stripping overlapping lines (Kα was used for most element) this ensures each element characteristic line was not interfered by another element signifying that fluorescence peak was specific to element analysed. Particle size effect (grain size) is one of the drawbacks of pressed powder pellet technique this was eliminated by pulverizing the samples to <10µm. Particle size effect was previously reported not to occur in samples with grain size below 400µm. [21] The use of multielement matrix-matching CRMs eliminates matrix effect due to absorption coefficient of transition elements and secondary fluorescence. One crucial limitation factor of FP method is its non-consideration of physical processes in the sample while FP method accuracy is heavily dependent on uncertainty of atomic parameters (particularly in low Z elements). Matrix- matching reference materials which mimic the physical characteristic of the sample subdue this effect in this analysis. The use of theoretical Kα lines eliminates the error arising from spectral distribution of the X-Ray tube using optimized analytical conditions (Table 1). The plot of CRMs and samples (Figure 2) reveal the the sample concentration fit within the CRMs linear range. Precision (repeatability and reproducibility) was statistically evaluated to account for FP method's systematic errors and sample preparation using pressed powder pellets technique described in

section 4.1 above. The precision of the method ranges from 0.003-1.10 for B20G and F231-A range from 0.001-1.52 as shown in Table 5. RSD values were less than 1.0 % except for SO_3 in all replicates, this is an indication of stability of instrument's goniometer – any deviation was due to sample preparation. Figure 1 depict the biplot of correlation of measured and theoretical intensity of the CRMs corrected for linearity hence using point that only improve the correlation as it will be used to develop the calibration plot for the measurement of samples, variation in concentration of CRM component is responsible for uneven spacing of the point on the graph. The correlation coefficient r in all the component of lateritic geological samples were above 0.98, US EPA criteria for FP method correlation coefficient (r > 0.95-0.97) for most elemnts. The standard error estimate (**σ_est)** were between 0.02 – 2.61 and the consistency of the of the techniques were satisfactory. The five laterite samples analyzed shows that the ranges of SiO_2 concentration was considerably high in F231-A and B20G (>30%) compared to KAWs, while Fe_2O_3 concentration was strikingly high in all the KAWs (>37%) compared to F231-A and B20G samples (< 37%). Al_2O_3 concentration was relatively high in all the samples (>30 %). All other component was below 1% except TiO_2 (>3.0%) and F231-A where its K_2O was 2.25% as depicted in table 5. WDXRF FP method has proven very viable approach in the analysis of lateritic component, this technique is inexpensive, fast, providing an accurate component of the laterites. Pressed pellets technique has a wide range of applicability in geological samples, this method was successful in eliminating matrix effects and theoretical overlap using few CRMs for the analysis of major and trace elements. considering the geological attributes of lateritic samples, the analysis result was consistent and reliable over long period of time. X-chart was established for the major element, but limit was not set due to heterogeneity of geological sample. Validation show reliability of the method from robust sample preparation.

Figure 2. Linear correlation plot of major component for CRMs and Samples





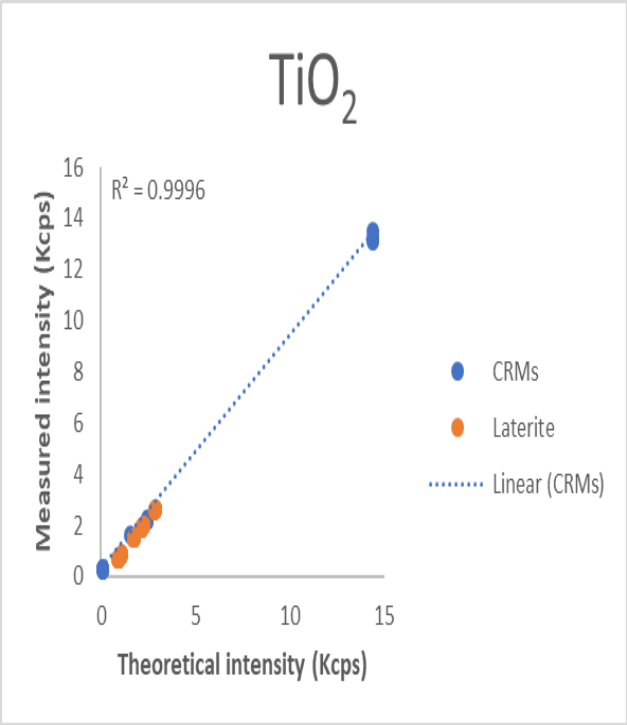


Table 5. Major element composition in Lateritic samples.

Samples (Mass %)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	SO_3	LOI=H_2O
B20G	45.811	0.912	32.250	11.049	0.212	0.138	0.057	0.048	0.113	0.065	0.020	9.19
F231-A	37.399	0.738	35.116	18.034	0.095	0.179	0.014	0.035	2.348	0.061	0.015	5.78
KAW014 B	1.672	2.064	49.239	20.427	0.004	0.000	0.002	0.082	0.066	0.001	0.053	26.24
KAW 014 C	1.696	1.616	35.323	42.406	0.015	0.000	0.000	0.060	0.013	0.006	0.101	18.45
KAW 014D	2.722	2.757	36.533	38.705	0.036	0.000	0.004	0.050	0.032	0.004	0.115	18.71

The trace element composition shows a marked variation in quantity in lateritic samples. KAW014C has the concentration of Chromium followed by KAW-014D while in Vanadium, it was reversed. Zirconium and Barium is most concentrated in F231-A followed by B20G which also more copper and Nickel than other samples. Rubidium, Tin and Strontium was higher in E231-A than other samples while B20G has the highest Zinc concentration followed by F231-A. Chlorine, Selenium, Yttrium, Niobium, Molybdenum, Antimony, Tellurium, Lead and Bismuth are below 100ppm in analysed samples as depicted in figure 3 below.

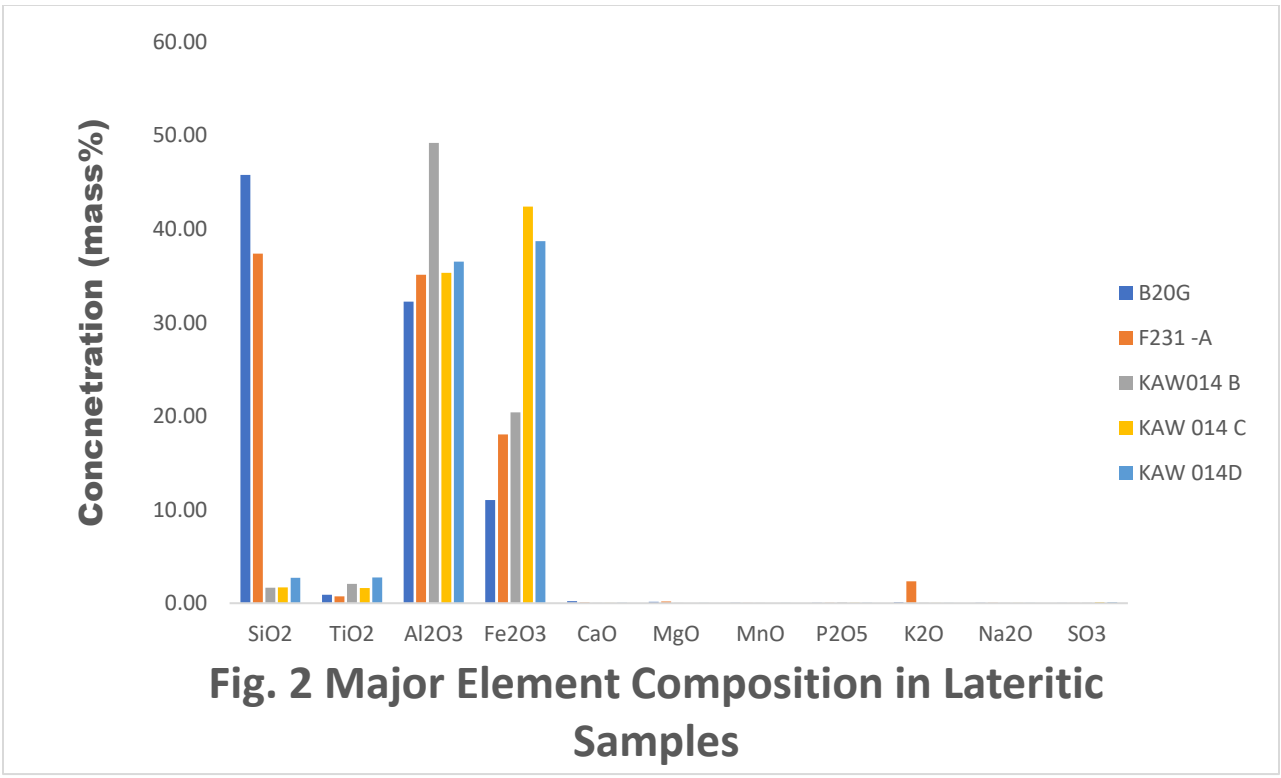


Fig. 2 Major Element Composition in Lateritic Samples

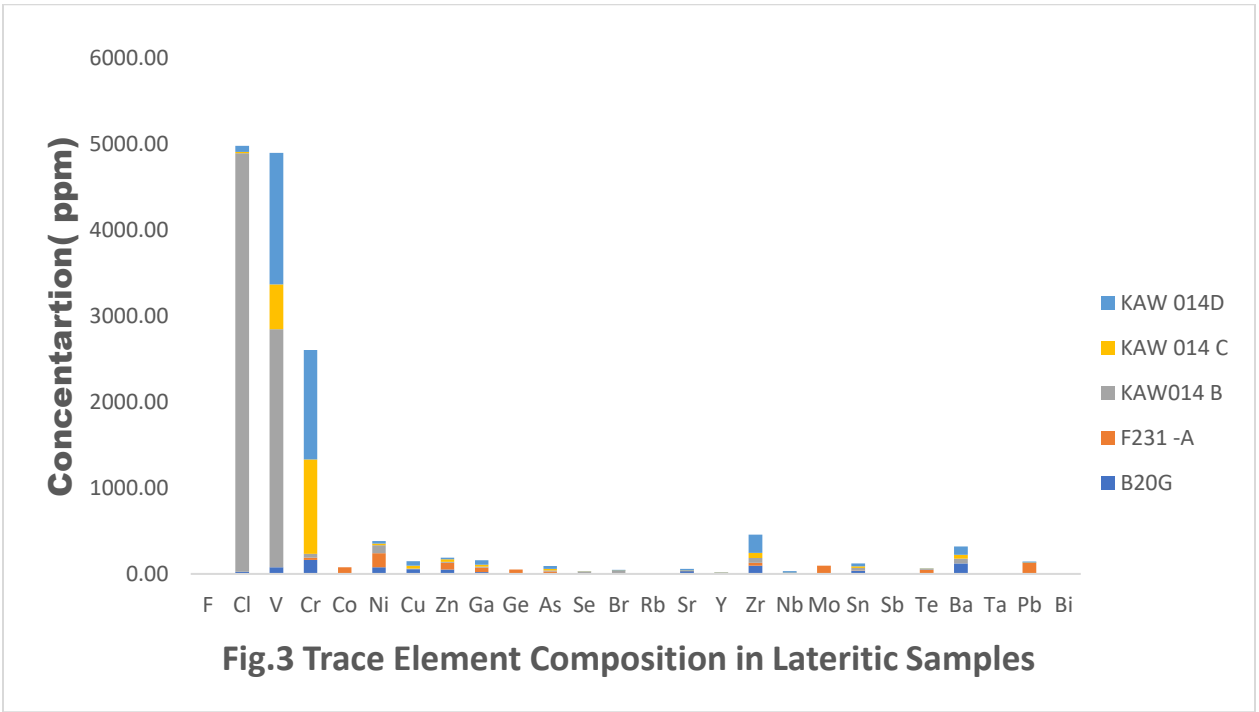


Fig.3 Trace Element Composition in Lateritic Samples

5.6 X-Control Charts

For the X-control charts, the parallel differences in analysis of samples were plotted against the on a chart to monitor within-Lab reproducibility. The chart can be described to be in a set-up phase hence mean range and limit of the control chart are not set. After collection of minimum of 10 data where values can be said to remain stable and were to be re-evaluated annually. Although the initial QC data offer no meaningful interpretation can deduced on the continuous performance of the method. It requires longer period of use to ascertain any change in the use of the method.

Figure 4 X- control chart of Silicate

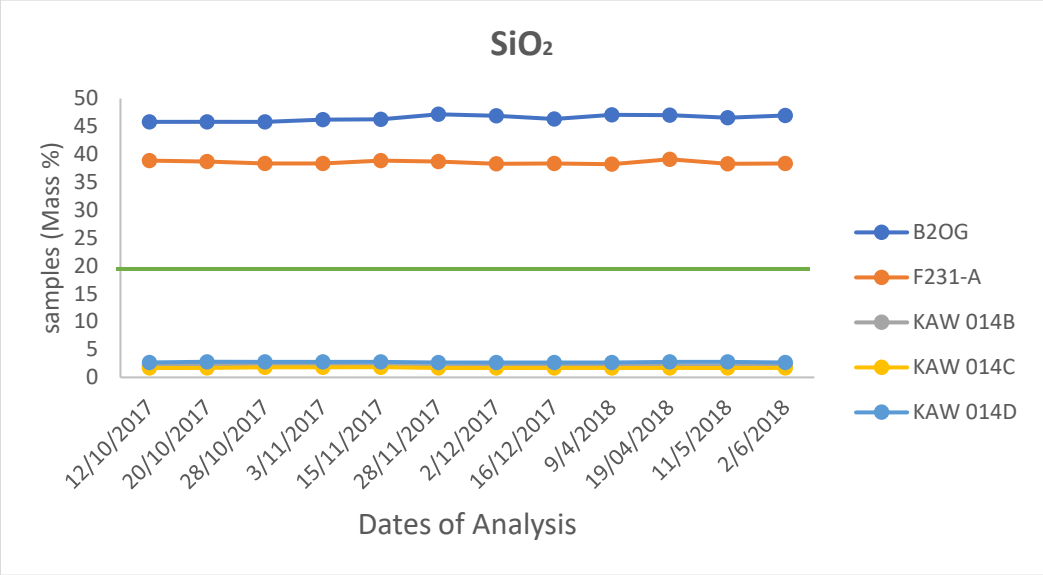


Figure 5 X- control chart of Titanium Oxide

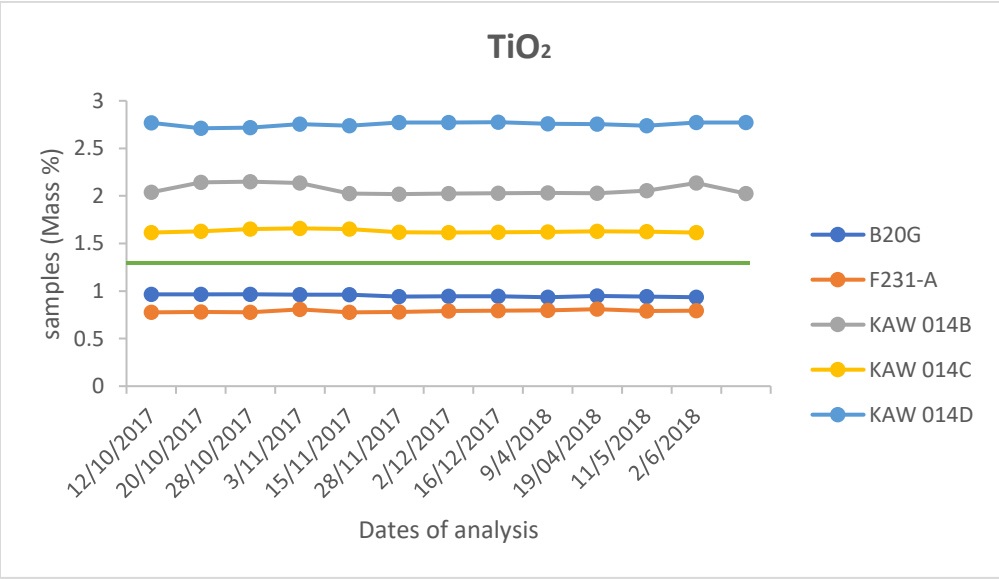


Figure 6 X- control chart of Aluminium Oxide

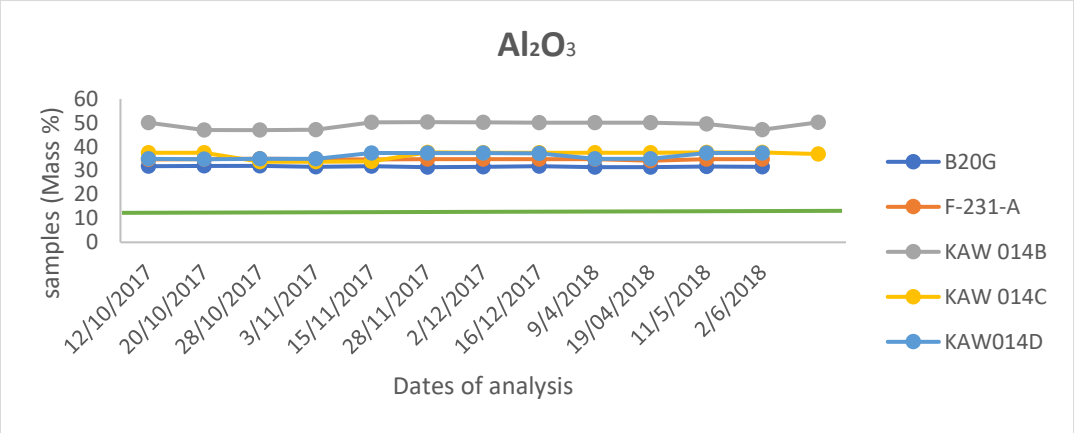


Figure 7 X- control chart of Iron (iii) Oxide

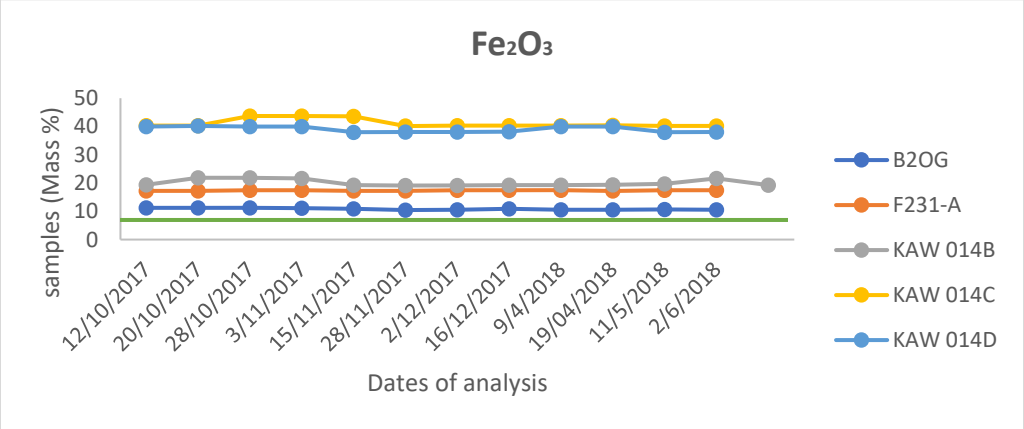


Figure 8 X- control chart of Calcium Oxide

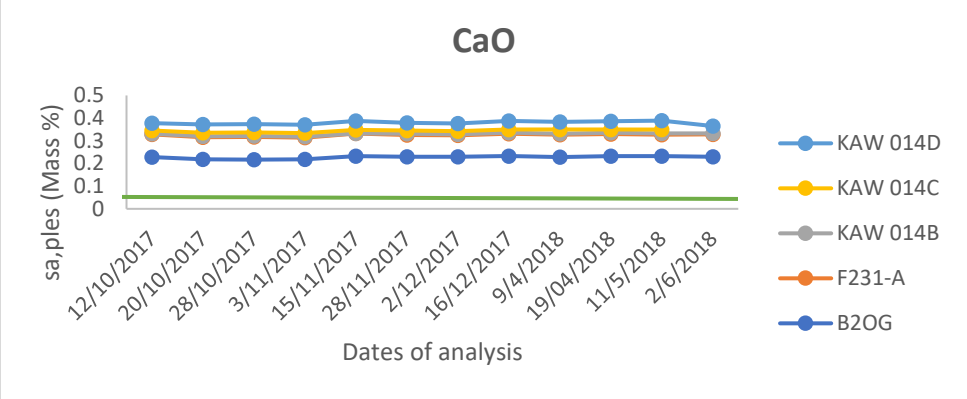


Figure 9 X- control chart of Magnesium Oxide

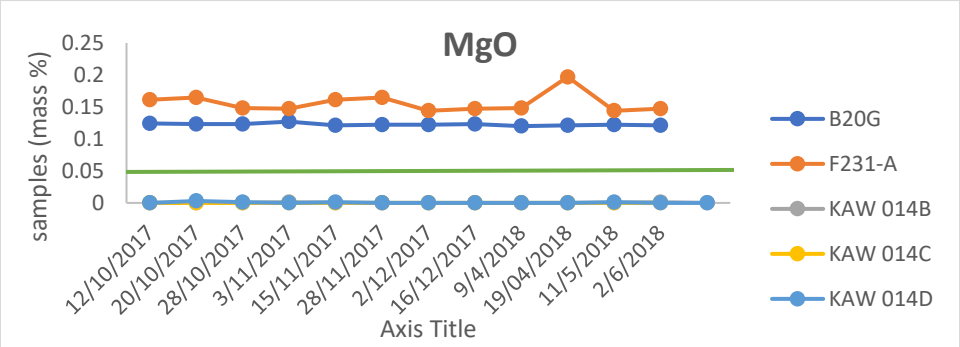


Figure 10 X- control chart of Manganese Oxide

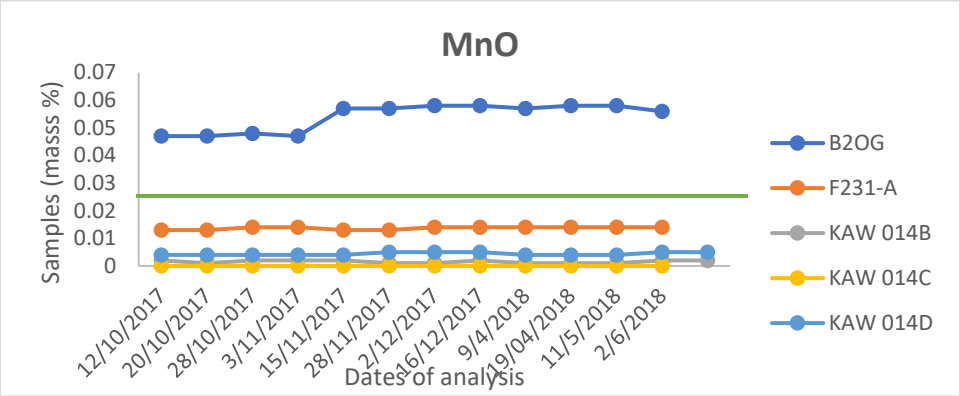
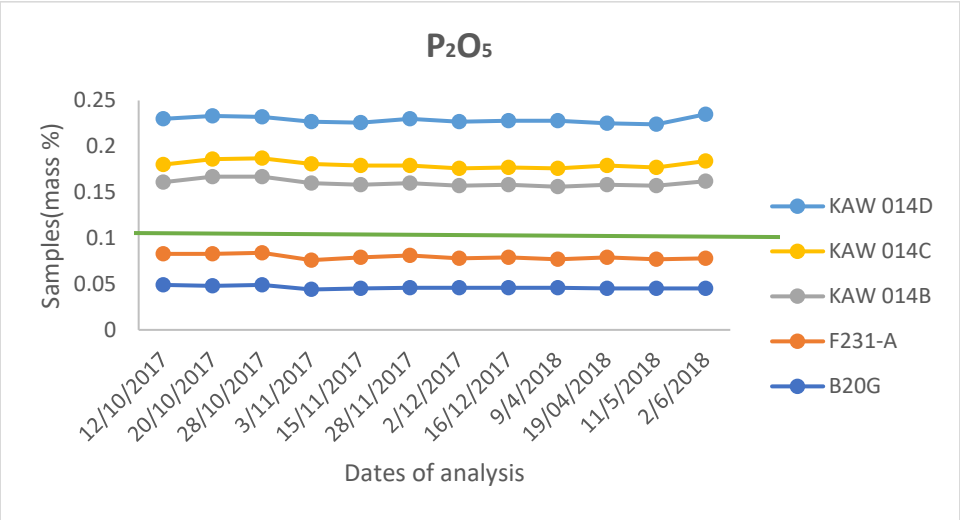


Figure 11 X- control chart of Phosphorus Pentoxide



Conclusion

FP-WDXRF method which is accurate and precise was developed and validated for the analysis of Fe-Al rich lateritic geological samples using pressed powder pellet technique. This method affords the use of least number of CRMs with same matrix composition for calibration. The correlation between the theoretical and measured intensities display good accuracy and the measured elements fit within the linear range. Validation of CRMS show reliability and consistency of the FP method while stability if the instrument governed by optimization of CRMs measuring conditions gave good repeatability with samples measured over a long time. This method is cheap rapid and can be easily adapted for routine quality control analysis.

Summary

Error Analysis of Fe-rich Geological Samples by X-ray Fluorescence Spectrometric Analysis: Fundamental parameter method

Rasheed Adeyemi Ishola

The purpose of this study was to develop and validate X-ray fluorescence spectrometry (XRF) method, the application of Fundamental Parameter method on Fe-rich geological samples major and trace elements, the analysis of pressed powder formulation. XRF is a widely used method of so-called non-destructive analysis of the chemical composition of various solids determination. XRF method is relatively simple and inexpensive but non-quantitative analysis was hampered by several problems, such as matrix materials, for example, variability in the composition of the mineral. During operation of the instrument measurement parameters were optimized to eliminate matrix effect, lines overlap and interference. The method used to evaluate three different Fe / Al-rich and the associated deposition laterite matrix compatible certified reference material into which the theoretical intensity of the analytical lines which were compared to the measured intensity of the subject, and from the calibration curve was developed in which the samples were quantitated. Fundamental parameters measured with the standards and the geological composition of the samples of unknown composition, and characterized by a variety of validation - accuracy, linearity, trueness, accuracy and uncertainty. The test method was used to estimate the uncertainty of the Nordtest which the composition of the standards measurements repeated on different days was evaluated in a systematic component and a random component.
Keywords: fundamental parameters method, laterite, XRF, Powder Formulation

Kokkuvõte

Vigade analüüs Fe-rikaste geoloogiliste proovide röntgenfluoresents spektromeetrilisel analüüsil fundamentaalparameetrie meetodil

Rasheed Adeyemi Ishola

Käesoleva uurimuse eesmärk oli välja töötada ja valideerida röntgenfluoresents spektromeeria (XRF) fundamentaalparameetrilise meetodi rakendus Fe-rikaste geoloogiliste proovide põhi- ja mikroelementide analüüsiks pressitud pulberpreparaatides. XRF on laialdaselt kasutatav nn mittepurustav analüüsimeetod erinevate tahkiste keemilise koostise määramiseks. XRF meetodi kasutamine on suhteliselt lihtne ja odav kuid kvantitatiivset analüüsi raskendavad mitmed välised probleemid nagu näiteks materjalide maatriksi mineraalse koostise varieeruvus. Töö käigus optimeeriti instrumendi mõõteparameetrid, et kõrvaldada maatriksiefekt, joonte kattumine ja interferents. Meetodi hindamiseks kasutati kolme erinevat Fe/Al-rikast lateriitset setendit ning nendega maatrikssobivaid sertifitseeritud referentsmaterjale milledel arvutati teoreetiline analüütiliste joonte intensiivsus mida võrreldi mõõdetud intensiivsuse suhtes ning töötati välja kalibreerimisgraafikud, millega proovid kvantifitseeriti. Fundamentaalparameetrite rakendusega mõõdeti standardite ja tundmatu koostisega geoloogiliste proovide koostis ning iseloomustati erinevate valideerimisparameetrite järgi - täpsus, lineaarsus, tõesus, täpsus ja mõõtemääramatus. Mõõtemääramatuse hindamiseks kasutati Nordtesti meetodit milleks hinnati standardite koostist selle korduval mõõtmisel erinevatel päevadel, hinnati süstemaatilist komponenti ja juhuslikku komponenti.

Märksõnad: fundamentaal parameetrite meetod, lateriit, XRF, pulber preparaat

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Annex 1 Instrumental Limit of Detection (ILODs) for analysed samples

B20G ez30		F231 269.4 A 1 ez30		KAW-14B ez30		KAW-14C ez30		KAW-14D ez30	
component	Detection Limit (mass%)	component	Detection Limit (mass%)	component	Detection Limit (mass%)	component	Detection Limit (mass%)	component	Detection Limit (mass%)
Na_2O	0.006	Na2O	0.007	MgO	0.009	MgO	0.009	MgO	0.008
MgO	0.006	MgO	0.006	Al_2O_3	0.018	Al_2O_3	0.015	Al_2O_3	0.015
Al_2O_3	0.009	Al_2O_3	0.010	SiO_2	0.007	SiO_2	0.005	SiO_2	0.007
SiO_2	0.017	SiO_2	0.017	P_2O_5	0.001	P_2O_5	0.001	P_2O_5	0.001
P_2O_5	0.001	P_2O_5	0.001	SO_3	0.001	SO3	0.001	SO3	0.001
SO_3	0.001	SO_3	0.001	Cl	0.002	Cl	0.002	Cl	0.002
Cl	0.002	Cl	0.002	K_2O	0.001	K2O	0.001	K_2O	0.001
K_2O	0.001	K_2O	0.002	CaO	0.001	CaO	0.001	CaO	0.001
CaO	0.001	CaO	0.001	TiO_2	0.005	TiO_2	0.005	TiO_2	0.008
TiO_2	0.006	TiO_2	0.004	V	0.004	V	0.003	V	0.004
V	0.002	V	0.002	Cr	0.003	Cr	0.003	Cr	0.003
Cr	0.002	Cr	0.002	Mn	0.002	Mn	0.003	Mn	0.002
Mn	0.001	Mn	0.002	Fe_2O_3	0.005	Fe_2O_3	0.008	Fe_2O_3	0.007
Fe_2O_3	0.003	Fe_2O_3	0.003	Ni	0.002	Ni	0.002	Ni	0.002
Co	0.001	Ni	0.001	Cu	0.001	Cu	0.002	Cu	0.001
Ni	0.001	Cu	0.001	Zn	0.001	Zn	0.002	Zn	0.001
Cu	0.001	Zn	0.001	Ga	0.001	Ga	0.001	Ga	0.001
Zn	0.001	Ga	0.001	Zr	0.004	As	0.001	As	0.001
Ga	0.001	As	0.000	Nb	0.001	Zr	0.005	Se	0.001
Rb	0.000	Rb	0.001			Nb	0.001	Br	0.001
Sr	0.000	Sr	0.000			I	0.008	Sr	0.001
Zr	0.002	Zr	0.002					Y	0.001
Nb	0.000	Nb	0.000					Zr	0.004
Ba	0.009	Sn	0.002					Nb	0.001
Pb	0.001	Ba	0.009					I	0.030
		Pb	0.001						

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